Hydrogen and Light Hydrocarbon Production from Logistic Fuels via Catalytic Cracking

Final Progress Report

Jae Ryu, Alan Zhou and Don Gobeille

June 24, 1996

U.S. Army Research Office

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1. Forward

Aspen Systems successfully developed an advanced fuel conversion process to produce a hydrogen-rich fuel gas stream from logistic fuels, such as cetane reference, diesel and JP-8, utilizing an innovative catalytic cracking technology. The overall objective was to develop a new fuel conversion process which operated at relatively low temperatures and pressures at high conversion efficiencies. In this program, we found that about 75 % and 63 % of the high heat value (% HHV) of the feedstock was recovered as C_4 and lighter hydrocarbons from the catalytic cracking of cetane reference fuel ($C_{16}H_{34}$) and No. 2 diesel, respectively. Hydrogen concentration in the effluent gas stream was more than 67 mol % (20 % HHV of the feedstock). In addition, we found that hydrogen sulfide (H_2S) was the only sulfur-bearing compound in the effluent gas stream.

Results of this research suggest that a number of crucial technical obstacles involved in current diesel reforming processes can be resolved by employing the catalytic cracking technology, including: (1) coking; (2) the desulfurization process; and (3) turndown ratio control. We believe that we may be able to overcome all these crucial technical chalenges in diesel reforming by employing the catalytic cracking technology.

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4.A. Statement of the Problem Studied

In the current diesel reforming technologies, three basic functions are involved to convert the diesel fuel to a purified hydrogen-rich gas stream: (1) conversion of the diesel fuel to H_2, CO_2, and CO; (2) shift conversion of CO through shift reaction with water to H_2 and CO_2; and (3) removal of sulfur-based contaminants. All the current diesel reforming processes have been designed to carry out these three basic functions in different processing conditions. As a result of intensive research efforts during the last two decades, a variety of diesel reforming processes have been developed. Numerous groups of engineers and organizations developed prototype diesel reformers for fuel cell applications. However, successful operation of fuel cells on diesel reformed gas stream has never been reported.

A number of crucial technical barriers have prevented the successful production of reliable and practical diesel reformers, regardless of the reforming process, these include: (1) coking; (2) the desulfurization process; and (3) startup procedures and turndown ratio control. We believe that we may be able to overcome all these crucial technical chalenges in diesel reforming by employing Aspen's catalytic cracking technology. Depending on the fuel reformer specifications, the diesel catalytic cracking unit can be used to produce a hydrogen-rich gas stream from diesel or can be used as a front end diesel processor.

The principal objective of the proposed program was to develop a catalytic cracking process to produce hydrogen and light hydrocarbon-rich gaseous stream from diesel. To accomplish this objective, Aspen Systems proposed a eight month program which encompassed following six technical tasks:

- Determine the cracking product distribution as a function of catalyst reactor temperature;
- Investigate the effect of water addition in the feedstock on the cracking product distribution;
- Investigate the effect of air addition in the feedstock on the cracking product distribution;
- Investigate the effect of hydrogen addition in the feedstock on the cracking product distribution;
- Determine sulfur mass balance via a complete analyses of sulfur content in the feedstock, cracked gas stream and catalysts;
- Perform a methanol steam reforming experiment utilizing Aspen's proprietary catalysts;and
- Fabricate and deliver a catalytic cracking unit with 5 lb/hr diesel fuel processing capability.

4.B. Summary of the Most Important Results

In this experimental research program, Aspen Systems successfully demonstrated the feasibility of producing a hydrogen rich gaseous stream from logistic fuels, such as No. 2 diesel, cetane reference fuel ($C_{16}H_{34}$), and JP-8, utilizing an innovative catalytic cracking technology. The overall objective of this program was to develop a new fuel reforming process which would operate at relatively low temperatures and pressures at high conversion efficiencies.

The cracking product gaseous stream contained 12-14 weight percent (w/o) of hydrogen, which was equivalent to 67 mol % of hydrogen, at a 700°C reactor temperature. We also found that more than 75 % and 63 % of the high heating value (% HHV) of the feedstock was recovered as C_4 and lighter hydrocarbons, including hydrogen, from the catalytic cracking of cetane reference fuel and No. 2 diesel, respecttively, at the 700°C reactor temperature. Adding air (up to carbon to oxygen ratios about 200; C/O>200) into the feedstock did not significantly affect the cracking performance of the zeolite catalysts. In addition, we found that hydrogen sulfide (H_2S) was the only sulfur containing compound in the cracking product gas stream. The catalytic cracking of JP-8 was not as easy as that of No. 2 diesel or cetane reference; we belived that the high aromatic concentration (17 %) and the relatively high concentration of light hydrocarbon constituents in the JP-8 were responsible for the relatively poor cracking performance, such as relatively low hydrogen concentration in the gaseous product and the low liquid to gas conversion efficiency, of the JP-8.

In summary, results of this research suggest that the catalytic cracking technology is a fundamental technological breakthrough that will provide a new opportunity to develop a compact, relatively simple and reliable fuel reformer to produce hydrogen and/or light hydrocarbons from logistic fuels for fuel cell operation. A number of crucial technical obstacles involved in current diesel reforming processes can be resolved by employing this technology, including:

- Fuel bound sulfur can be readily removed from the gas phase at relatively low temperatures (below 700°C) and near ambient pressures without using air or water in the feedstock;
- The heavy petroleum distillates in diesel, which usually lead to coking in ordinary diesel reforming processes, can be easily converted to light hydrocarbons without coking. We believe that reforming light hydrocarbons (C_4 or lighter) should be easier than reforming diesel;
- This technology offers a very wide turn down ratio (about 8.5:1), which is important in achieving a high overall system efficiency in both idle and full power operations of a power generation system; and
- The entire reforming process can be established at low temperatures (below 700°C) and with far less demand in air and water; therefore, reformer system peripherals can be greatly reduced in size and complexity.

4.B.1. Experimental Procedures

Experimental Setup

The main objective of the proposed research was to experimentally demonstrate the feasibility of producing hydrogen and light hydrocarbon molecules from various logistic fuels utilizing a catalytic cracking process. For this experiment, we established a fixed bed reactor apparatus, as shown in **Fig. 1**. This setup consisted of: (1) a fuel feed system; (2) a reactor unit; (3) a liquid hydrocarbon condenser unit; and (4) a sampling and chemical analysis unit.
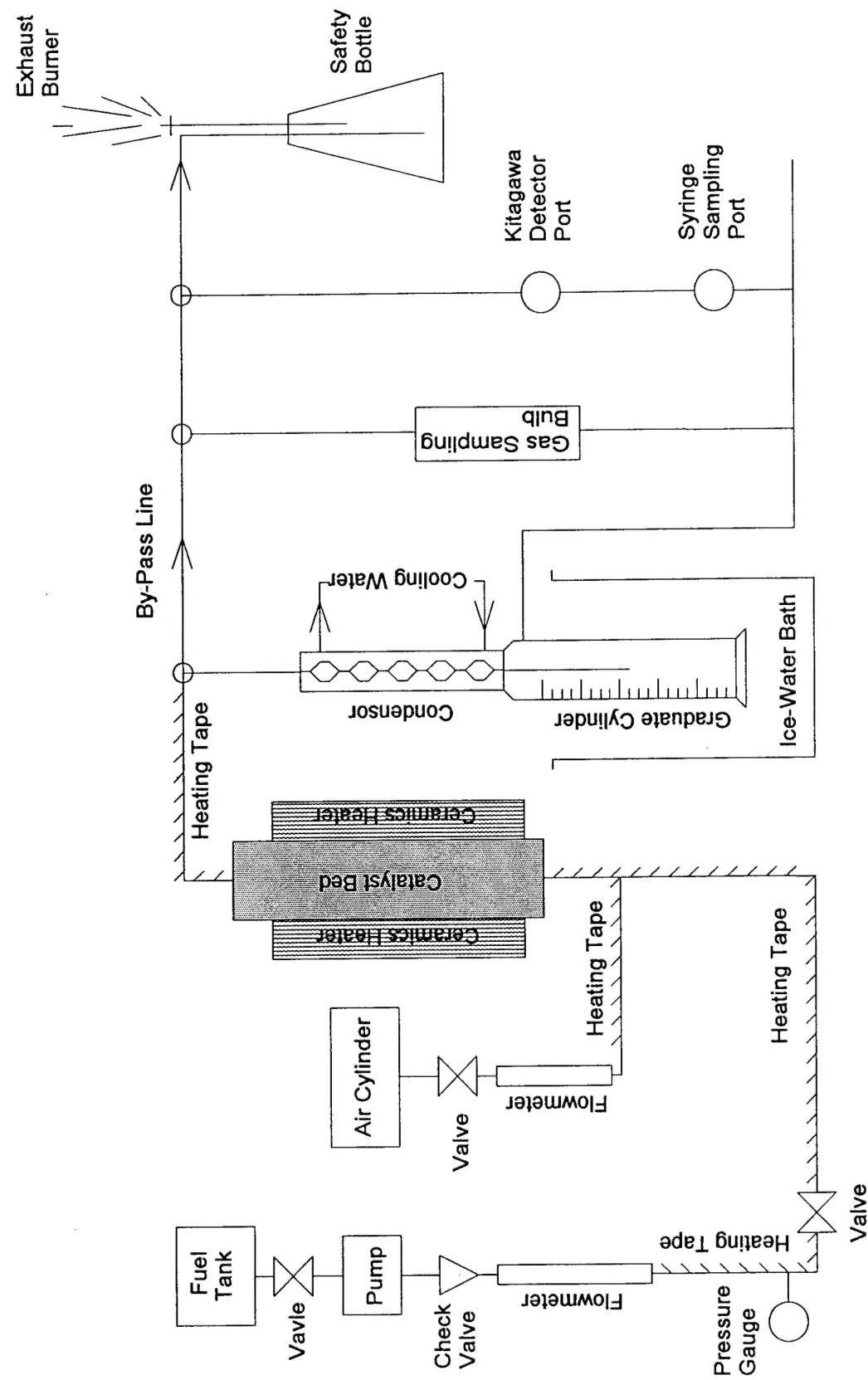
Figure 1: Schematic of the Catalytic Cracking Experiment Setup.

The fuel was fed using a liquid metering pump (LMI Model No. J051-191), and fuel flow rates were controlled by using a pre-calibrated liquid rotameter (Omega Model No. FL-3210ST). Air was supplied from a compressed cylinder, and air flow rates were controlled by using a pre-calibrated gas rotameter (Matheson Model No. R7640). For mass balance analysis, accurate control and measure of the flow rate of the feedstock, particularly fuel flow rates, was a very important experimental parameter. Surprisingly, the flow rates of the No. 2 diesel and JP-8 were very different at a given settings of the rotometer, as shown in **Fig. 2**. We believe the difference in flow rates is due to a difference in the viscosities of the fuels. The specifications of the fuels used in this research are listed in **Table I**.

The reactor unit consisted of a stainless steel tube (3/4 inch OD and 12 inches long), a high temperature ceramic heater (6 inches long), a pre-heater tape, and tape heaters for effluent line temperature control. The temperature of the reactor was controlled by a programmable temperature controller and a type K thermocouple located on the outside of the reactor tube. The actual temperature of the catalyst bed was not monitored directly; however, according to our previous experience, the catalyst bed temperatures were generally 120-150°C lower than those of the reactor set temperatures (depending on the fuel flow rates).

In this research, center breaking, pentasil cracking catalysts[1] (HZSM-5 zeolite) were used as the primary cracking catalysts. We found from the previous research (supported by U.S. Army Natick RD&E Center) that this catalyst was not promoting coking in diesel cracking, and its cracking performance was not affected by the sulfur content in the feed.[2] In order to increase the hydrogen concentration in the product gas stream, we also investigated the effect of
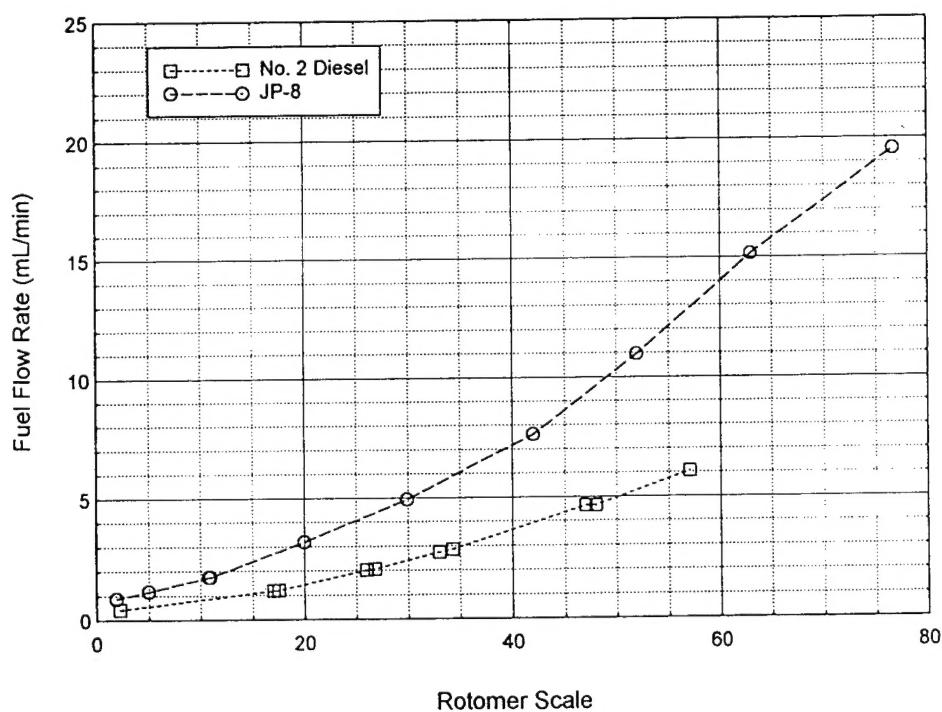
Figure 2: JP-8 and No. 2 Diesel Fuel Flow Rate Calibration Curves.

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Table I: Type of Fuel Used and Their Specifications.

Fuel	Supplier	Properties	
Technical Grade Cetane (n-Hexadecane, $C_{16}H_{34}$)	Humphrey Chemical Co.	Flash Point (°C)	135
		Auto Ignition Temperature (°C)	394
		Boiling Point (°C)	287
		Specific Gravity	0.77
No. 2-D Diesel	Exxon	Flash Point (°C)	52
		Sulfur Content (w/t)	0.03
		Distillation Temperature, 10-90% (°C)	282-338
		Specific Gravity	0.88
		Kinematic Viscosity at 40°C (cSt)	1.9-4.1
JP-8	Phillips Chemical Co.	Flash Point (°C)	46
		Sulfur Content (w/t)	0.18
		Distillation Temperature, 10-90% (°C)	190-294
		Specific Gravity	0.8
		Kinematic Viscosity at 20°C (cSt)	1.98
Methanol, 99%	Aldrich		
Ethanol, denatured	Aldrich		

faujasite cracking catalysts[3] (HY zeolite) addition to the pentasil catalysts on the catalytic cracking reactions. In a preliminary experiment, we did not find any positive result of adding the faujasite catalysts; therefore, most of the experiments were conducted using the pentasil cracking catalysts only. Generally, 50 cm^3 of catalyst was packed into the stainless steel reactor tube at fuel flow rates of 50-108 cm^3/hr; the volume space velocity of the catalytic cracking reactions employed in this research ranged between 1 and 2 cm^3/hr/cm^3.

The catalyst bed temperature (determined by the ceramic heater temperature) is the most important variable in the catalytic cracking experiments. In this program, we selected the reactor temperatures of 500°C, 600°C and 700°C for heavy hydrocarbon fuels (cetane, No. 2 diesel, and JP-8) and 100°C, 200°C and 300°C for methanol and ethanol. Temperatures for the tape preheater and effluent line heater were controlled using variable power supplies, and monitored by using type K thermocouples and temperature indicators. The preheater temperature was generally set at 250°C. The temperature of the effluent gas line was set at 300°C-350°C.

Cracking Product Analysis

The effluent gas stream from the catalyst reactor was introduced into a condenser unit, which consisted of a water cooling condenser and a graduated cylinder liquid collector. The temperature of the cooling water was about 20°C (tap water) and the graduated cylinder liquid collector was immersed into an isothermal bath, of which the temperature was kept at near 0°C using ice during liquid collection. All the heavy hydrocarbons, we believed, were captured and condensed in the collector; therefore, constituents in the effluent gas stream from the condenser unit would be only permanent gas or light hydrocarbons of which the boiling point was above 0°C. The effluent gas stream passed through a GC sampling unit and a water safety bottle, and vents through a flame exhaust.

The gas sampling unit consisted of a gas sampling glass bulb with PTFE valves and a positive seal injection port, a Kitagawa tube H_2S analysis port, and a syringe adapter port. When the reactor conditions and the fuel flow rate reached steady-state in about 30 min, the effluent stream from the reactor was introduced into a cold trap. The effluent stream from the cold trap was then introduced to the gas sampling unit. After about an hour in this mode, we started analyzing the gas phase samples. There are three steps in gas phase sampling and analysis; first, 5 cm^3 of the gas sample was taken from the effluent gas stream using a syringe adapter port and injected to GC for permanent gas analysis. Then, H_2S concentration in the gas stream was measured using a Kitagawa tube at the Kitagawa tube analysis port. Finally, 125 cm^3 of the gas sample was taken, using the gas sampling glass bulb for hydrocarbon distribution analysis at the University of Kentucky. All the gas sampling and analysis ports were located serially at the down stream of the cold trap.

Products of the catalytic cracking reaction potentially have many hundred chemical compounds and a wide range of product distribution, from hydrogen and permanent gases to light and heavy hydrocarbons (C_1-C_{32}). Positive identification and quantification of the numerous peaks emerging from GC columns were time consuming. Therefore, we classified the hydrocarbon products based on their carbon numbers and quantified them. For this simplified product analysis, we still had to use five different GC's, and numerous combinations of a variety of detectors and separating columns to analyze the cracking products from one reaction. The GC columns and detectors employed in this research are listed in **Table II**.

In general, product analysis at Aspen Systems was designed for testing many samples qualitatively to optimize the catalytic cracking conditions. Product analysis at the University of Kentucky (Professor B. Davis' group at the Center for Applied Energy Research) was designed for quantitative analysis of the cracking products.

After collecting the liquid phase for a certain time period (the duration of the cold trap operation depended upon an accumulation rate of the liquid phase), the volume of the liquid phase in the condenser bottle was measured to determine fuel-to-gas phase conversion efficiency. The conversion efficiency was determined using the volume balance (see equation 1) between the amount of fuel feed (the fuel flow rate times period of cold trap operation) and the amount of liquid remaining in the condenser bottle after heating it to room temperature overnight.

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Table II: GC Columns and Detectors Employed for Cracking Product Analysis

GC	Column	Detector	Product of Interest	Remarks
Varian 3300	60/80 Carboxen-1000	TCD	Permanent gases	at Aspen
	HayeSep Q	TCD	C_1-C_3	at Aspen
HP 5890 A	SPB-1, 5μm film, capillary column	FID	C_3-C_{15}	at Aspen
HP 5890 II	DB-5 capillary column	MS	C_1-C_{32}	at UK
Carle 311H	Carboxen	MS	C_1-C_7	at UK
Carle 311H	Carboxen	TCD	Hydrogen	at UK
HP 5985 A	Chromosorb T	FPD	Sulfur gases	at UK

$$\text{Conversion Efficiency (\%)} = \left(1 - \frac{V}{F \times t}\right) \times 100 \qquad (1)$$

where F is the fuel flow rate (cm³/min), t is the period of cold trap operation (min), and V is the volume of the remaining liquid in the condenser bottle after heating it to room temperature (cm³). In this calculation, we assume that the density of the liquid fuel and the liquid residue in the condenser are the same. Actually, the liquid phase product consisted of unsaturated olefins and exhibited a lower density than that of the fuel. Therefore, the actual conversion efficiency should be higher than what was measured.

Upon completion of the catalytic cracking experiment, all feedlines, such as fuel and air (if it was used), were closed, and the reactor unit was cooled to room temperature. During the reactor cooling, the bent line (exhaust line) was left open because the fuel remained in the feedlines and the reactor cracked during cooling from high temperatures. In any case, we did not employ any catalyst regeneration treatments after each run. Usually, we operated the catalytic cracking unit 4-6 hrs a day, depending on the length of the liquid phase collection time. After each catalytic cracking operation, experimental conditions and results were logged into a computer. A typical log-chart is shown in **Fig. 3**.

4.B.2. Results

Catalytic Cracking of Cetane

Complete analysis of the cracking products distribution (or mass balance) are one of the most important technical issues in this research. We have conducted product distribution analysis for samples from cetane, diesel, and JP-8 cracking experiments. Detailed procedures for the product distribution analysis will be described in this section using data obtained from cetane cracking (technical grade: 93% $C_{16}H_{34}$, from Humphrey Chemical Co.).

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Run ID	RUN96129A	RUN96130A	RUN96223A	RUN95C19B	RUN95C19A	RUN95C18B	RUN95C20B
Type of Run	A700-D10-A30	A700-D10-A30	A700-D10-A30	A700-D10-O05	A700-D10-O10	A700-D10-O20	A700-D10-O30
Catalyst ID	CAT96108	CAT96108	CAT96220	CAT95C15	CAT95C15	CAT95C15	CAT95C15
Page in Notebook	944	945	962	920	919	918	922
Temp. of Preheater	308	315	308	315	315	317	310
Fuel Flow Rate (scale)	10.1	10.3	8.5	10.3	9.6	10.2	10.7
Fuel Flow Rate (ml/min.)	0.8	0.8	0.7	0.8	0.8	0.8	0.8
Water Flow Rate (scale)	/	/	/	/	/	/	/
Water Flow Rate (ml/min.)	/	/	/	/	/	/	/
Air Flow Rate (scale)	Air=30	Air=30	Air=30	Oxygen=5	Oxygen=10	Oxygen=20	Oxygen=30
Air Flow Rate (ml/min.)	10	10	10	0.5	2	6	10
Collecting Time (min.)	264	275	246	129	120	122	144
Cold Trap Oil at 0°C (ml)	98.0	99.0	76.0	44.0	36.0	45.0	47.0
Cold Trap Oil at R.T. (ml)	98.0	99.0	76.0	44.0	36.0	45.0	47.0
Cold trap Water (ml)	/	/	/	/	/	/	/
Water Conversion (%)	/	/	/	/	/	/	/
Conversion at 0°C (%)	54.1	56.1	56.8	58.4	61.5	54.7	61.4
Conversion at R.T. (%)	54.1	56.1	56.8	58.4	61.5	54.7	61.4
$H_2O/C_{16}H_{34}$ Mole Ratio	/	/	/	/	/	/	/
H_2S Concentration (ppm)	197	216	240	190	140	170	155
Gas Phase Sample							
Remark	Repeat of RUN96104A	Repeat of RUN96104A					

Figure 3: A Typical Log-Chart for Catalytic Cracking Experiments.

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In GC analysis, we identified more than 200 hydrocarbon compounds in the liquid phase (more than 99% of them are unsaturated olefin) and gas phase (mixture of alkanes and alkenes) samples. For simplicity of analysis, we categorized them only in a carbon number base. Using the known values of the molar weight and the density of the individual hydrocarbon (base on paraffin data), the measured volume (or weight) of the liquid phase collected, and the product distribution (in weight percent) obtained from GC analysis, we calculated actual mol numbers of the hydrocarbons. Mol number distribution of the hydrocarbons in the gas phase sample was also calculated using a similar procedure. In this calculation, the actual mol number of olefins (hence number of carbon atoms) in the cracking products would be slightly greater than calculated value because of the molar weight difference between olefin and paraffin.

Using the mol number distribution calculated above, we calculated the number of carbons/Avogadro's number and the heating values of the hydrocarbons in the cracking products. Results of these analyses are plotted in **Fig. 4**. As shown in this figure, the dominant cracking products were propane and propylene at reactor temperatures of 500°C and 600°C. At the 700°C reactor temperature, the dominant cracking product was methane with relatively high concentrations of ethane and propane. Remarkably, the product distributions of 500°C and 600°C cracking were almost identical. At all reactor temperatures, about 20 % HHV, which corresponded to 53.6 % of total hydrogen in the feed, was recovered as hydrogen molecules in the gas phase.

Results of the analysis for cetane cracking are summarized in **Tables III** and **IV**. As shown in **Table III**, total number of carbons in the cracking product is about 89% of the total number of carbons in the feedstock. It is possible that the 11% deficiency in total carbon number may be due to coking. However, considering that there was almost complete recovery in the heating value (see **Table IV**), the carbon loss via coking did not occur during catalytic cracking. We believe that the molar weight difference between olefin and paraffin hydrocarbons may be responsible for the carbon deficincy, as illustrated in the following paragraphs.

The total carbon number of the cracking product (mainly olefins) was calculated using following equation:

$$C.N._n = (W_n/M_n) \bullet n \qquad\qquad (2)$$

where $C.N._n$ is a number of carbon/Avogadro number for a hydrocarbon molecule with an n carbon number (C_nH_{2n+2} paraffin), W_n is the weight of the molecule with the carbon number n, M_n is the molecular weight of the C_nH_{2n+2}, and n is a number of carbon in the molecule C_nH_{2n+2}. In this calculation, the n is a known value and the W_n is a measured value from the GC analysis. However, we use M_n by assuming the molecular weight of the olefin, M_{n-xH}, is the same as the molecular weight of the paraffin; this assumption will introduce a significant error in the mole number calculation, and hence the total carbon number calculation. Since M_n is always greater than M_{n-xH} ($M_n > M_{n-xH}$), the calculated carbon number $C.N._n$ is always smaller than actual carbon number $C.N._{n-xH}$ for the olefin products. Therefore, the actual "% total carbon in product/total carbon in feedstock" would be higher than the reported values in **Table III**. The experimental conditions employed and results obtained on cetane cracking are summarized in **Table V**.

HHV Product Distribution
(Cetane)
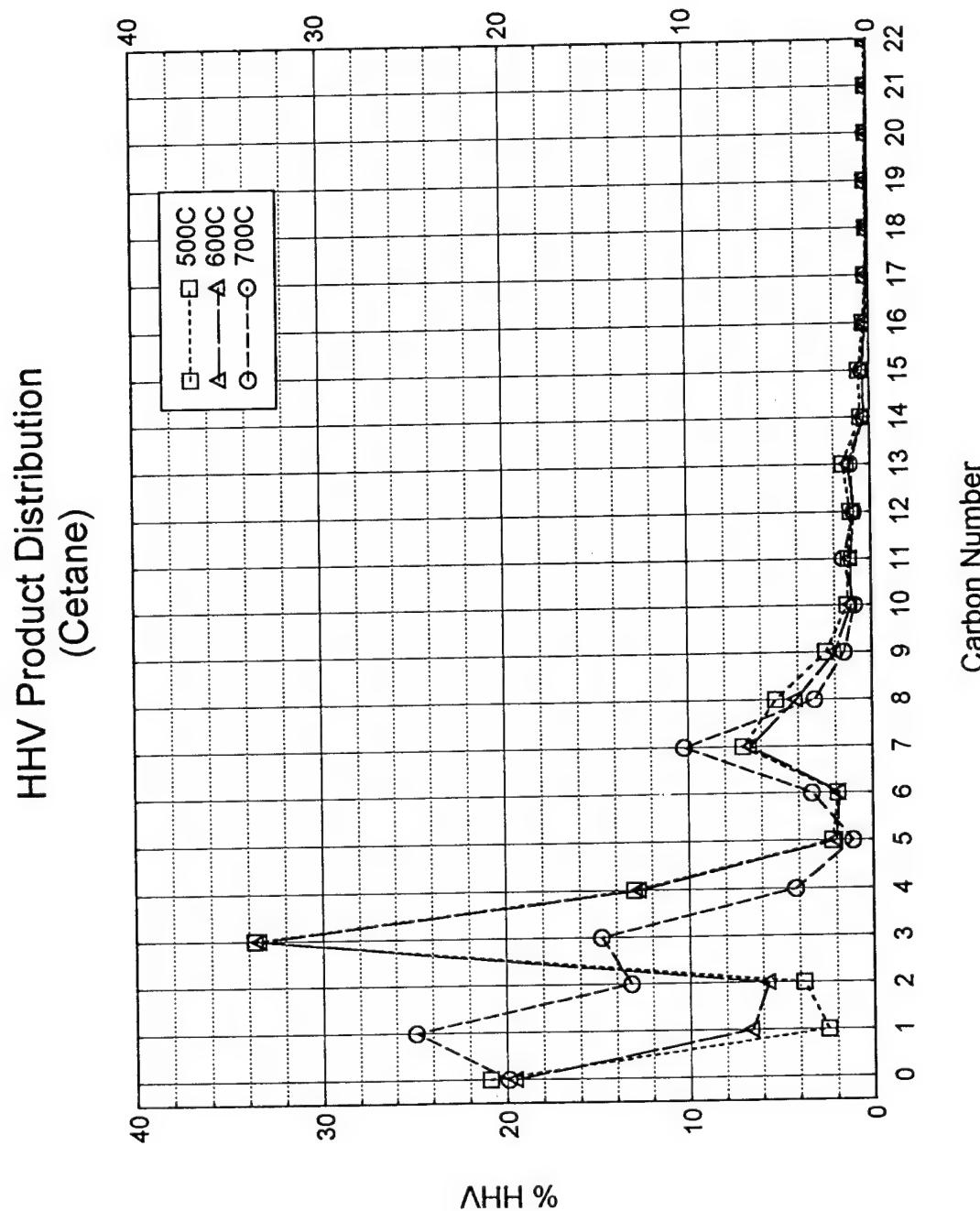
Figure 4: % HHV Product Distributions for Cetane Cracking.

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Table III: Mass Balance -- Carbon Number

Run ID	Reactor Temp. (°C)	Carbon No./AV			% Total Carbon/ Feedstock
		Liquid Phase	Gas Phase	Total	
96227A	500	0.01	0.03	0.04	88.8
96221A	600	0.01	0.03	0.03	88.9
96220A	700	0.01	0.03	0.03	87.1

Table IV: Mass Balance -- High Heating Value (HHV)

Run ID	Reactor Temp. (°C)	Feedstock HHV	Product HHV	% Recovery
96227A	500	31.47	29.99	95.3
96221A	600	24.5	23.72	96.8
96220A	700	24.5	24.28	99.1

Table V: Summary of Cetane Cracking Study

Run ID	Feedstock & Reactor Conditions	Conv. % (v/o)	H_2 Conc. in gas phase (w/o)	HHV Recoverd (%)		
				H_2	C_4 & Lighter	C_8 & Lighter
96220A	0.7cm³/min Cetane, 700°C	78	11.3	19.9	75.3	92.6
96221A	0.7cm³/min Cetane, 600°C	78	11.1	19.5	78	92.4
96227A	0.9cm³/min Cetane, 500°C	70	13.1	20.9	73.9	90.2

Catalytic Cracking of Diesel

The diesel cracking product distributions and the carbon number distribution of the diesel itself are shown in **Fig. 5**. In this figure, we conveniently divided the product distribution into three different regions based on carbon numbers. The first region contained carbon numbers from zero (hydrogen) to four (butane). Products in this region were a mixture of paraffins and olefins, and were a gas phase above room temperatures. In this region, the fraction of light hydrocarbons increased with an increase in reactor temperature. For example, the concentrations of methane

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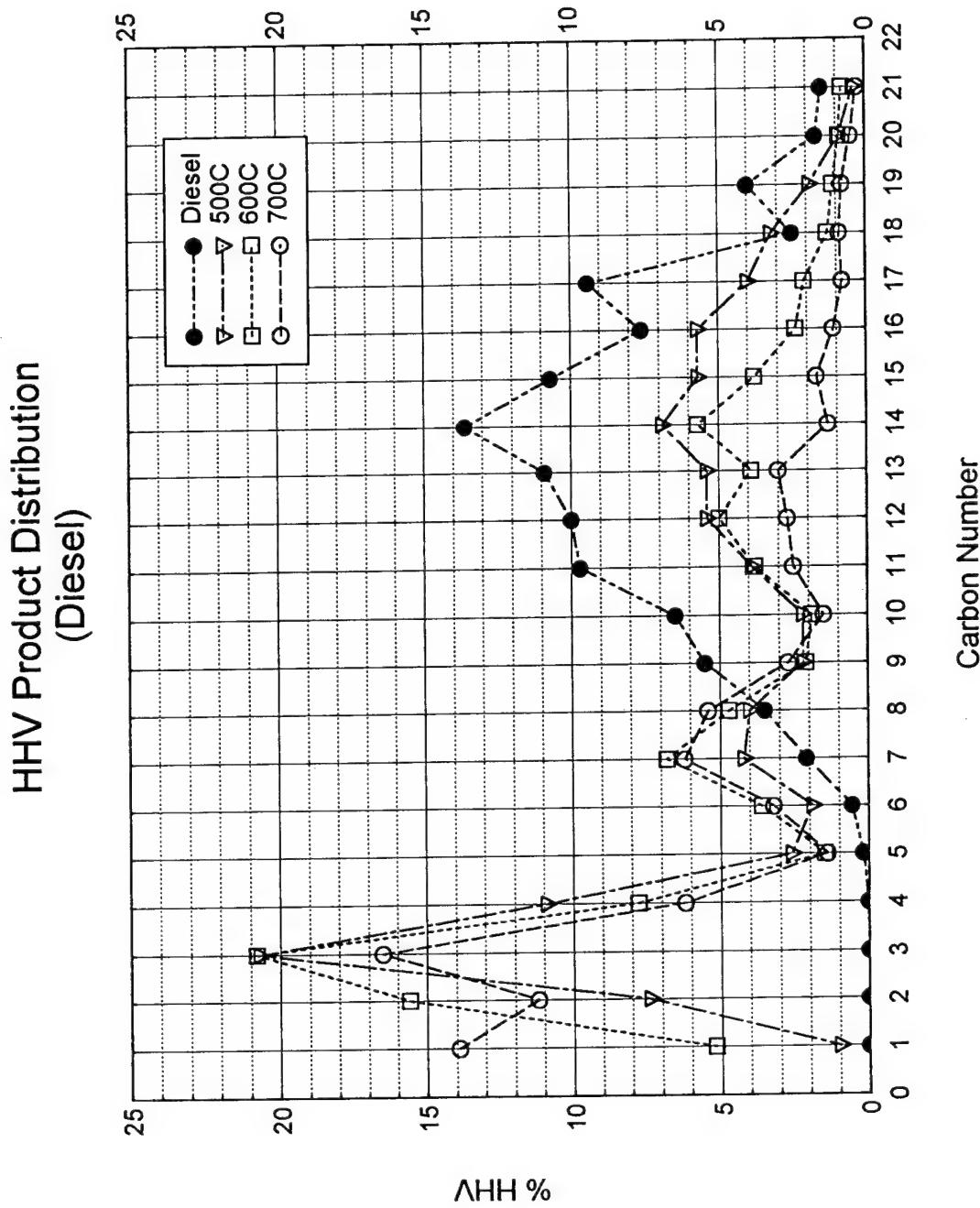
Figure 5: % HHV Product Distributions for Diesel (No. 2) Cracking.

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in the cracking products were 1, 5.2, 13.7 % HHV for the reactor temperatures of 500, 600, and 700°C, respectively.

The second region contained a carbon number between C_6 and C_9. Products in this region were all olefins. A small hump in product distributions (increase in product yield) in this region (C_6 - C_9) was observed in the cracking of any heavy hydrocarbons investigated in this research. We also observed that the yield for C_6 - C_9 hydrocarbon products increased as the reactor temperature increased. It is well known that pentasil cracking catalysts, which were used in this research, promote a high yield of C_6 and C_7 hydrocarbons in the petroleum industrial hydrocracking process.

The third region contained carbon numbers greater than C_{10}. Cracking product distributions in this region generally followed the hydrocarbon distribution of the feedstock itself. For a given carbon number, the feedstock consisted of paraffins and olefins, the cracking products, however, consisted of olefins only. This result might indicate that the appearance of heavy hydrocarbons in the cracking product was not due simply to the channeling of fuel through the catalyst bed. In addition, the amount of heavy hydrocarbons ($>C_{10}$) in the cracking products decreased significantly as the reactor temperature increased. At a 700°C reactor temperature, the total amount of heavy hydrocarbons was only 16 % HHV of the feedstock.

The effects of air in the feedstock on the catalytic cracking of diesel is also interesting. The diesel cracking product distributions with and without air in the feedstock at a 700°C reactor temperature are shown in **Fig. 6**. In this reaction, flow rates for diesel and air were 0.7 and 10 cm³/min, respectively, which corresponded to a carbon to oxygen atomic ratio (C/O) of 224. As shown in this figure, heavy hydrocarbon (C_9 and higher) product distributions were almost identical with and without air. In the lighter hydrocarbon side, however, the product distribution was somewhat affected by adding air into the feedstock; particularly, hydrogen concentration in the product was relatively sensitive to air concentration (carbon to oxygen ratios) in the feedstock. For example, the hydrogen concentrations in the cracking products were 16.4 and 21.1 % HHV without and with air (C/O=224), respectively. The effects of air addition in the feedstock on the catalytic cracking reaction will be discussed at greater length in later sections. The experimental conditions employed and results obtained on diesel cracking are summarized in **Table VI**.

Catalytic Cracking of JP-8

The dominant hydrocarbon components in JP-8 are in the carbon number C_{10}-C_{13}, which are lighter hydrocarbons than that of the No. 2 diesel (C_{11}-C_{17}). According to the manufacturer's specifications, JP-8 also contains approximately a 17 w/o of aromatics. These factors make JP-8 more difficult to break, via the catalytic cracking, into hydrogen and gaseous components.

As shown in **Fig. 7**, the dominant JP-8 cracking products in any catalytic cracking conditions were C_3 and C_4. As the reactor temperature increased from 500°C to 700°C, the fraction of heavy hydrocarbons decreased dramatically and hydrogen concentrations in the product gradually increased. The JP-8 to gaseous fuel conversion efficiency was very low at the

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Table VI: Summary of Diesel (No. 2) Cracking Study

Run ID	Feedstock & Reactor Conditions	Conv. % (v/o)	H$_2$ Conc. in gas phase (w/o)	HHV Recoverd (%)		
				H$_2$	C$_4$ & Lighter	C$_8$ & Lighter
95B24A	0.8cm^3/min Diesel, 700°C	58.8	12.07	16.4	63.4	80.8
96129A	0.8cm^3/min Diesel+ 10cm^3/min Air, 700°C	56.1	14.5	21.1	62.1	82.2
95C15A	0.8cm^3/min Diesel, 600°C	43.1	N/A	N/A	49.4	66.1
95C22B	0.9cm^3/min Diesel, 500°C	39.9	N/A	N/A	40	52.7

### HHV Product Distribution (700C)
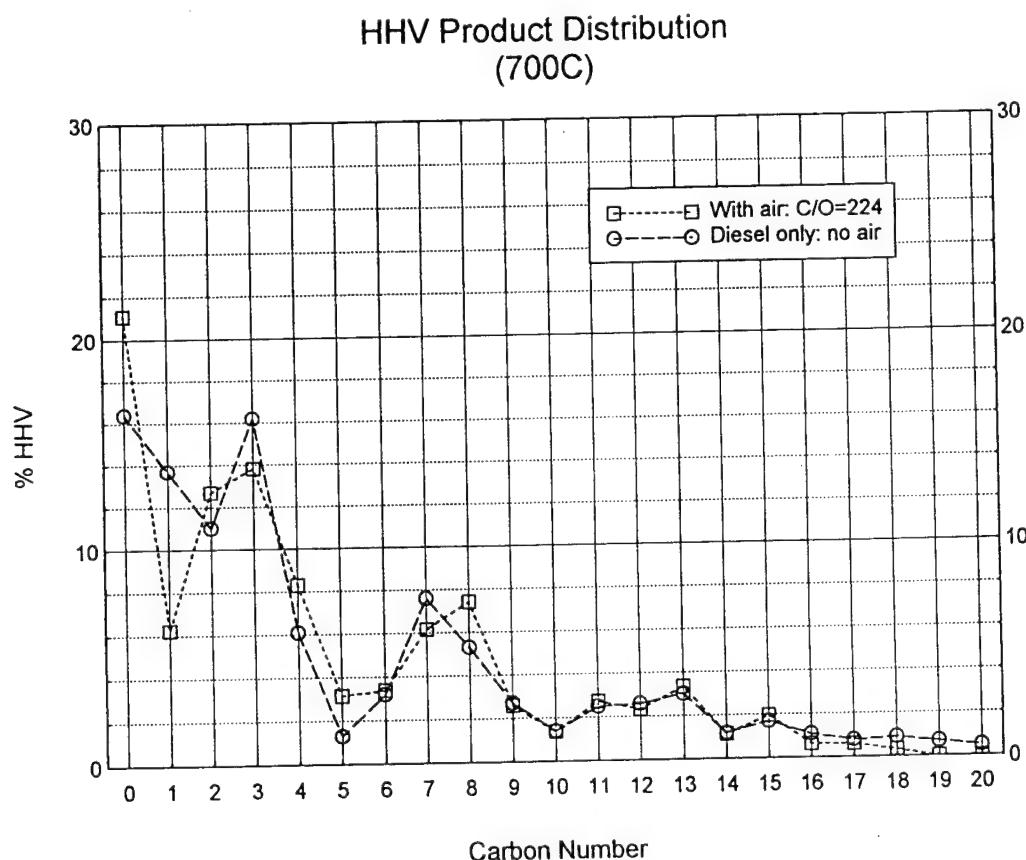
Figure 6: % HHV Product Distributions for Diesel (No. 2) Cracking with and without Air in the Feedstock.

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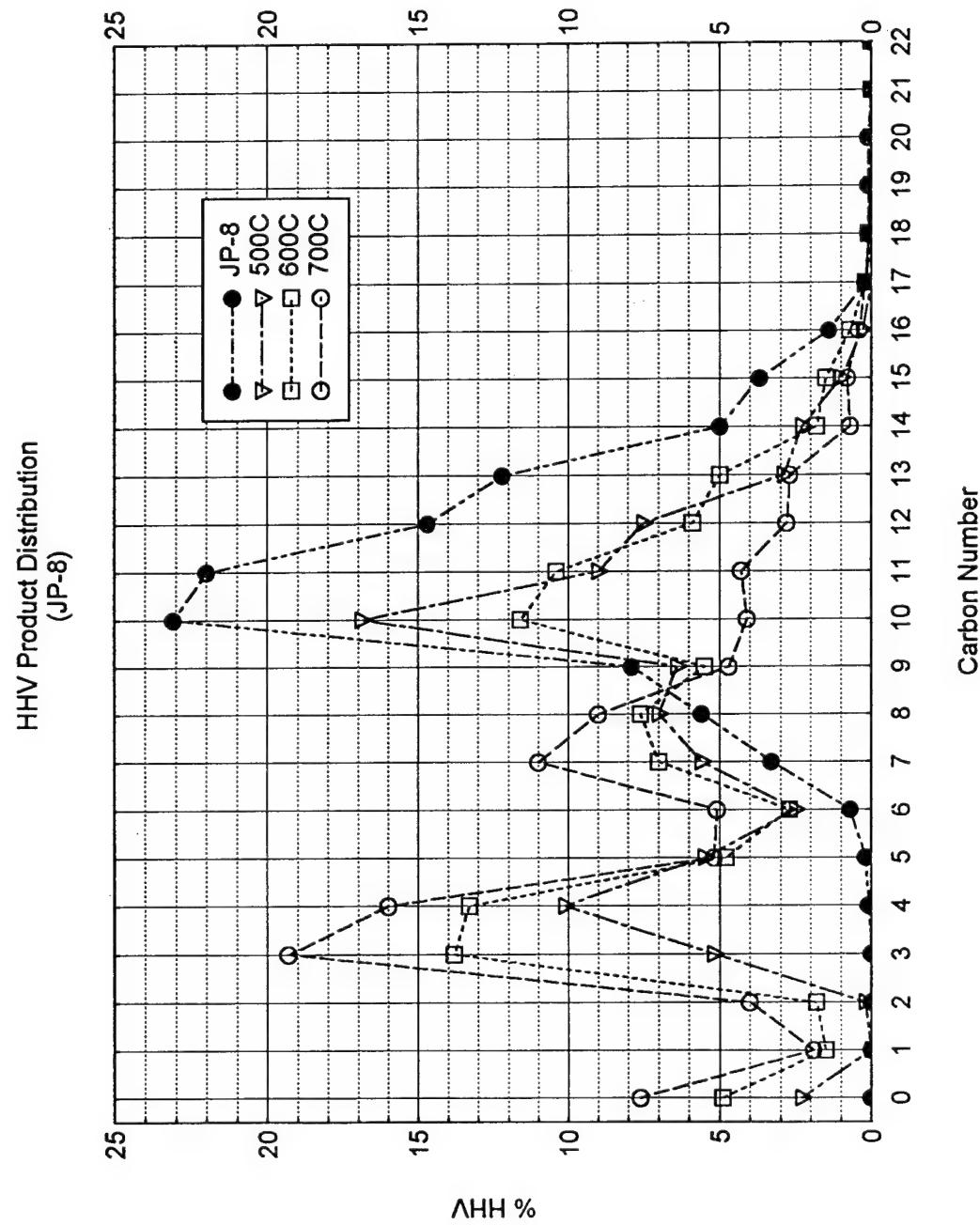
Figure 7: % HHV Product Distributions for JP-8 Cracking.

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low reactor temperature (19.8 %), but gradually increased as the reactor temperature increased (46.8 % at 700°C, see **Table VII**). Initially, we suspected that high sulfur content (1800 ppm sulfur) might responsible for the relatively poor results in JP-8 cracking. However, we did not find any physical evidence of catalyst poisoning, such as accumulation of sulfur in the catalysts, after cracking of JP-8. Therefore, we believed that the high concentration of aromatics and light hydrocarbon components in JP-8 were responsible for the poor cracking performance of JP-8.

Cracking of Methanol and Ethanol

Considering the high catalytic activity of zeolite catalysts toward the hydrocarbon processing, it is interesting to investigate the catalytic reaction of methanol and ethanol over these catalysts. It is hard to imagine that a cracking reaction, such as a carbon chain-center breaking reaction in heavy hydrocarbons, will occur in these fuels with only one or two carbons in a molecule. In any case, we found very interesting results in these experiments, which will be briefly described in the following paragraphs.

The experimental conditions employed and results obtained on methanol/ethanol cracking experiments are summarized in **Table VIII**. As shown in this table, the main products were water and liquid hydrocarbons. In the methanol experiments, the total volume of the feedstock (methanol) and the total volume of the liquid phase products (water+liquid hydrocarbons) were almost the same. The GC analysis results indicated that the liquid hydrocarbons consisted of C_5-C_{12} hydrocarbons and their components were very similar to that of the high quality (high octane rating) gasoline on the market (see **Table IX**). Although it was an interesting result for other applications, such as production of gasoline from biomes or natural gas, we can't use this technology to produce hydrogen. Therefore, we did not pursue further research on ethanol or ethanol cracking in this program.

Table VII: Summary of JP-8 Cracking Study

Run ID	Feedstock & Reactor Conditions	Conv. % (v/o)	H$_2$ Conc. in gas phase (w/o)	HHV Recoverd (%)		
				H$_2$	C$_4$ & Lighter	C$_8$ & Lighter
96320A	1.6cm^3/min JP-8+ 2cm^3/min Air, 700°C	46.8	5.5	7.6	48.8	79.1
96320B	1.8cm^3/min JP-8+ 2cm^3/min Air, 600°C	27.8	5.9	4.9	35.2	57.3
96328A	1.7cm^3/min JP-8+ 2cm^3/min Air, 500°C	19.8	5.5	2.31	17.83	38.5

Table VIII: Summary of Methanol and Ethanol Cracking Study

Feedstock	Reactor Temperature (°C)	Total Volume of Feedstock (cm³)	Total Volume of Liquid Phase Product (cm³)	Total Volume of Water (cm³)	Total Volume of Liquid Hydrocarbon (cm³)
Methanol	200	188.4	194.2	133.8	60.4
	300	194	190.7	126.2	64.5
Ethanol	200	201.6	81.8	81.8	0
	300	527.8	156	132	24

4.B.3. Discussion

Air in the Feedstock

Cracking of heavy hydrocarbons to produce light hydrocarbons has been practiced for almost two hundred years in the petroleum and coal industries. However, the exact mechanism involved in catalytic cracking of hydrocarbons is not precisely known, although a staggering amount of research has been published[4-6] on the effect of catalysts, operational variables, and feedstock quality on product yields, to name just a few. When cracking occurs, there is a hydrogen deficiency in the reaction, and complex reactions follow in order that the unsaturated light hydrocarbons may be reconciled; reactions that may occur include polymerization, formation of aromatic hydrocarbons, and coking. Most of these secondary reactions of light olefins are undesirable and reduce the yield of gaseous products (C_6-C_{10}). The degree of these secondary reactions, which will determine the product distribution in the cracking process, depends heavily on process conditions. Furthermore, addition of various cracking promoters or product stabilizers, such as water, air, or hydrogen (recycled from the product stream), can significantly suppress the aforementioned secondary reactions.

Air in the feedstock may promote the catalytic cracking reaction via stabilizing unsaturated cracking products, and/or may eliminate free carbon radicals from a reaction zone. The free carbon radicals may react with other hydrocarbon radicals via complex reactions, such as polymerization and aromatic hydrocarbon formation, and/or may deposit onto the catalyst surface and deactivate it. In any case, presence of the free carbon radicals would not be beneficial for the production of hydrogen or lighter hydrocarbon molecules, which is the primary goal of this research. Air may also react with hydrogen and demote catalytic cracking reactions by removing hydrogen in the reaction zone. Thermodynamically, the oxygen-carbon reaction would be more favorable than the oxygen-hydrogen reaction in the temperature ranges of this research (500°C-700°C). However, experimental results indicated that the hydrogen oxidation reaction might be favorable if carbon to oxygen ratios in the feedstock were less than 200 (C/O < 200).

Table IX: Composition of the Liquid Phase Hydrocarbons from Methanol Cracking at 200°C.

Compounds	Weight Percent (w/o)
Propene	0.26
i-Butane	1.35
i-Butene+1-Butene	1.78
t-2-Butene	0.75
c-2-Butene	0.55
i-Pentane	3.75
t-2-Pentene	1.51
c-2-Pentene	0.69
2-Methyl-2-Butene	3.48
2-Methylpentane	3.17
3-Methylpentane	1.17
Hexene	1.42
Benzene	1.28
Toluene	7.81
Ethylbenzene	1.63
m+p-Xylene	16.1
o-Xylene	4.59
1-Ethyl-3-Methylbenzene	3.1
1-Ethyl-4-Methylbenzene	1.72
1,2,3-Trimethylbenzene	0.91
1,3,5-Trimethylbenzene	7.97
4-Carbon Benzene	1.16
Unidentified	balance

We also found that the conversion percentage and the hydrogen concentration were easily duplicable by adding air to the feedstock in the C/O ratio ranges between 200 and infinite (no air in the feedstock). In this region, hydrogen concentrations in the cracking product were not greatly affected by the amount of air in the feedstock. There was a trace amount of water detected in the product stream when the C/O ratios were higher than 200 in the feedstock, but water was not accumulated in the condenser bottle. When the C/O ratios were less than 200 in the feedstock, water began accumulating in the condenser bottle, and the hydrogen concentration in the product decreased (excessive air).

In summary, air in the feedstock at the C/O ratios about 200 and higher was beneficial to obtain duplicable results in the catalytic cracking process. An increase in the amount of air (C/O < 200) resulted in low hydrogen concentration in the product, low liquid to gas conversion, and water condensation. We believed that excessive oxygen in the feedstock removed hydrogen, a valuable reactant in catalytic cracking of hydrocarbon, from the reaction zone.

Water in the Feedstock

In any catalytic cracking conditions investigated in this research, the net reaction was more favorable for water formation than for water consumption. Therefore, the exact amount of water in the feedstock was recovered in the product. Although we did not know the reaction paths of the water in the catalytic cracking reactor, we could not find any positive or negative effects of water on the catalytic cracking of heavy hydrocarbons over the zeolite catalysts. Therefore, we stopped the water effect study after five test runs.

Sulfur Issue

Fuel bound sulfur poisons or deactivates reforming and shift catalysts, and ultimately deactivates fuel cell catalysts if allowed to reach the fuel cell. In a conventional diesel reforming process, fuel-bound sulfur is removed using a zinc oxide reactor after converting it to H_2S at relatively high temperatures (850-1000°C). Although sulfur can be removed via this conventional desulfurization process, the high process temperatures unfortunately promote coking. In addition, the high process temperature is undesirable due to the reactor material's comparability, process control, and waste energy issues.

In the previous research supported by the U.S. Army Natick RD&E Center, we found that a sulfur content of 2500 ppm in the fuel would not affect the catalytic cracking performance of the zeolite catalysts.[2] In the current program, we also found no evidence of sulfur poisoning on catalysts. Furthermore, H_2S was the only sulfur containing compound in the gas phase hydrocarbons. In this case, we could easily remove H_2S using a scrubber in the effluent gas stream. Overall, about 70 weight percent of fuel-bound sulfur was converted to H_2S at a 700°C reactor temperature without adding any conversion promoters, such as hydrogen or air, to the feedstock.

H_2S concentration in the diesel cracking product stream, as functions of the reactor temperature and carbon to oxygen ratio (numbers in parentheses), is shown in **Fig. 8**. The H_2S concentration was determined by using Kitagawa tubes. Generally, as the reactor temperature increased, the H_2S concentration in the product gas stream decreased. For any given reactor temperature, the H_2S concentration in the product stream increased as the carbon to oxygen ratio in the feedstock increased.

In summary, catalytic cracking of heavy hydrocarbons over the zeolite catalysts was not affected by the sulfur concentration in the fuel. In addition, we can convert fuel bound sulfur into H_2S in the fuel gas stream at relatively low temperatures and at ambient pressure. The H_2S in the gas stream can be easily removed by utilizing an existing sulfur removal technology.

Hydrogen Concentration in the Cracking Product

A dependable and simple way to produce hydrogen from logistic fuel is a crucial technology for the successful development of a compact and high power density fuel cell power systems. In this research, we found that a significant amount of hydrogen was produced in the cracking reaction, as shown in **Fig. 9**. In this figure, the letter and number in the parentheses refers to types of fuel used (C: cetane, D: diesel, and J: JP-8) and carbon to oxygen ratio, respectively.

In cetane cracking, hydrogen concentration was about 11-13 w/o (greater than 60 mol %) of the gas phase in the cracking product. A high hydrogen concentration was also obtained in the diesel cracking product. For example, at a 700°C reactor temperature, we routinely produced 11-14 w/o (or 60-70 mol %) of hydrogen in the gas phase, which represented more than 50 % of the hydrogen in the feedstock. Generally, diesel cracking with or without air in high C/O ratios resulted in high hydrogen concentration in the product. As air content in the feedstock increased (low C/O ratios), the hydrogen concentration in the product decreased, probably due to hydrogen oxidation. On a few occasion, the measured hydrogen concentration was relatively low at the high C/O. We believed that the inconsistancy in the hydrogen concentration in the cracking product was due to problems involved in gas sampling procedures rather than inconsistencies in the cracking reactions.
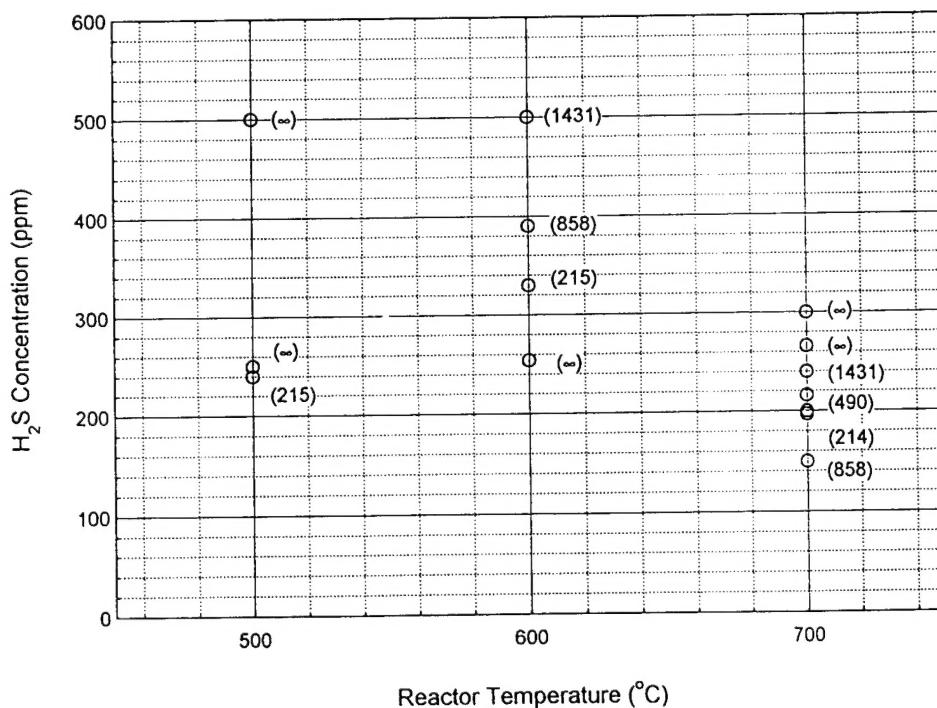

Figure 8: **H_2S Concentration in the Diesel Cracking Product Gas Stream as Functions of Reactor Temperature and Carbon to Oxygen Ratio (Numbers in Parentheses).**

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The hydrogen concentration in the JP-8 cracking product was about 5-6 w/o, which was significantly lower than those of diesel or cetane reference fuel. We believed that the high concentration of aromatics (17 %) and relatively light hydrocarbon constituents in the JP-8 were responsible for the low hydrogen concentration in the JP-8 cracking product. Aromatic hydrocarbons generally contain a small amount of hydrogen in their molecules, such as benzene (C_6H_6), therefore, they could not release any hydrogen atoms or molecules during cracking. In addition, a strong double carbon bond in the aromatic molecules might prevent them from participating in the catalytic cracking reactions.
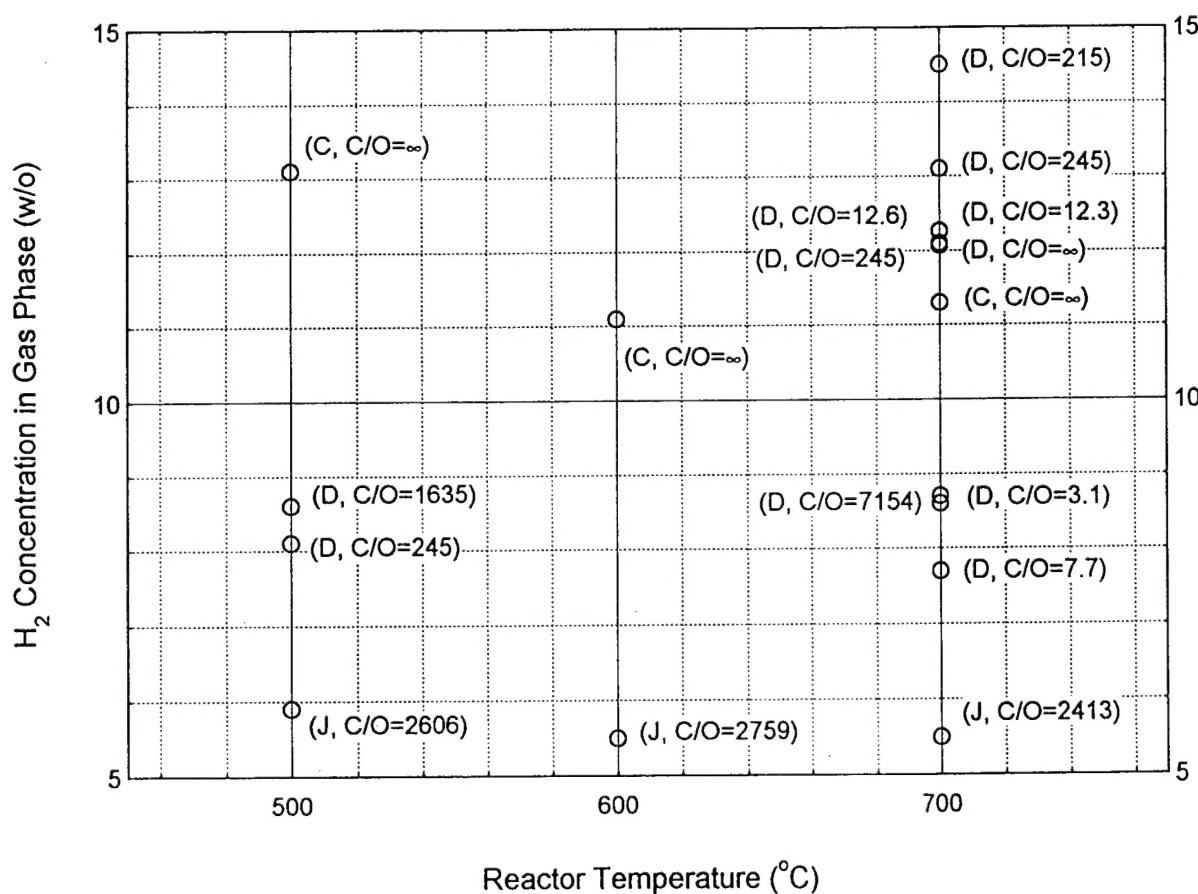
Figure 9: **H_2 Concentration in the Cracking Product Gas Stream as Functions of Reactor Temperature, Types of Fuel (Letter in Parentheses), and Carbon to Oxygen Ratio (Numbers in Parentheses).**

4.B.4. Conclusion

Aspen Systems successfully demonstrated the feasibility of producing a hydrogen rich gaseous stream from logistic fuel via a catalytic cracking process. The cracking product gaseous stream contained 12-14 w/o of hydrogen, which was equivalent to 67 mol % of hydrogen. H_2S was the only sulfur containing compound in the gas phase product. Adding air to the feedstock (C/O>200) did not affect cracking performance of the zeolite catalysts; however, water was condensed at the product stream when air content was high in the feedstock (C/O<200).

Results of this innovative research provide a new opportunity to develop a compact and dependable fuel reformer to produce hydrogen from logistic fuels for fuel cell operation. A number of crucial technical problems involved in the current diesel reforming technology, such as the desulfurization process, coking, and the turndown ratio control, can be resolved easily by employing the Aspen's catalytic cracking technology.

4.C. List of Publications and Technical Reports

None

4.D. List of Personnel Earned Advanced Degrees

None

5. Report of Inventions

A simple method of producing hydrogen rich gas stream from heavy hydrocarbons -- Invention disclosure filed at Aspen Systems, Inc.

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13. ABSTRACT (Maximum 200 words)

Aspen Systems successfully developed an advanced fuel conversion process to produce a hydrogen-rich fuel gas stream from logistic fuel, such as cetane reference, diesel and JP-8, utilizing an innovative catalytic cracking technology. The overall objective was to develop a new fuel conversion process which operated at relatively low temperatures and pressures at high conversion efficiencies. In this program, we found that about 75 % and 63 % of the high heat value (% HHV) of the feedstock was recovered as C_4 and lighter hydrocarbons from the catalytic cracking of cetane reference fuel ($C_{16}H_{34}$) and No. 2 diesel, respectively. Hydrogen concentration in the effluent gas stream was more than 67 mol % (20 % HHV of the feedstock). In addition, we found that hydrogen sulfide (H_2S) was the only sulfur-bearing compound in the effluent gas stream. A number of crucial technical obstacles involved in current diesel reforming processes can be resolved by employing this technology, including: (1) coking; (2) the desulfurization process; and (3) turndown ratio control. We believe that we may be able to overcome all these crucial technical chalenges in diesel reforming by employing the catalytic cracking technology.

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